

US-PAT-NO: 4797187

DOCUMENT-IDENTIFIER: US 4797187 A

TITLE: Semi-permeable membranes prepared via reaction of cationic groups with nucleophilic groups

DATE-ISSUED: January 10, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Davis; Thomas E.	Lafayette	CA	N/A	N/A
Schmidt; Donald L.	Midland	MI	N/A	N/A
Kau; Jee I.	Concord	CA	N/A	N/A
Wessling; Ritchie A.	Midland	MI	N/A	N/A
Whipple; Sharon S.	Sanford	MI	N/A	N/A
Fibiger; Richard F.	Midland	MI	N/A	N/A
Pickelman; Dale M.	Auburn	MI	N/A	N/A

ASSIGNEE INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE
The Dow Chemical Company	Midland	MI	N/A	N/A	02

APPL-NO: 07/086123

DATE FILED: August 17, 1987

PARENT-CASE:

CROSS-REFERENCE TO RELATED APPLICATION

This is a divisional of Application Ser. No. 790,287, filed Oct. 22, 1985, now U.S. Pat. No. 4,704,324, which is a continuation-in-part of Application Ser. No. 719,037, filed Apr. 3, 1985, now abandoned, which is a continuation of Application Ser. No. 313,051, filed Oct. 19, 1981, now abandoned, which is a continuation-in-part of Application Ser. No. 162,356, filed June 24, 1980, now abandoned.

INT-CL-ISSUED: [04] C05B007/00

INT-CL-CURRENT:

TYPE	IPC	DATE
CIPS	B01D67/00	20060101
CIPS	B01D71/40	20060101
CIPS	B01D71/00	20060101
CIPS	B01D69/00	20060101
CIPS	B01D69/12	20060101
CIPS	B01D69/14	20060101
CIPS	B01D71/44	20060101
CIPS	B01D71/46	20060101
CIPS	B01D69/08	20060101
CIPS	B01D71/52	20060101
CIPS	B01D71/72	20060101
CIPS	B01D71/68	20060101
CIPS	B01D71/80	20060101
CIPS	B01D71/82	20060101

US-CL-ISSUED: 204/180.2 , 204/180.9 , 204/181.1 , 204/181.4 , 204/296  
, 427/245 , 427/301 , 427/333 , 521/27 , 521/28 , 521/31  
, 521/32 , 521/33

US-CL-CURRENT: 427/58, 204/296 , 204/486 , 204/507 , 427/245 , 427/301  
, 427/333 , 521/27 , 521/28 , 521/31 , 521/32 , 521/33  
, 96/12 , 96/13

FIELD-OF-CLASSIFICATION-SEARCH: 204/296; 204/180.2 ; 204/180.9 ;  
204/181.1

; 204/181.4 ; 204/181.6 ; 204/181.7 ; 521/28  
; 521/27 ; 521/31-33 ; 427/243 ; 427/245  
; 427/301 ; 427/333 ; 264/340

**\*\*See application file for complete search history\*\***

REF-CITED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>2676166</u>	April 1954	Webers	260/85.7
N/A			N/A

<u>2891025</u>	June 1959	Price	260/29.6	N/A
N/A				
<u>3078259</u>	February 1963	Hatch et al.	260/79.7	N/A
N/A				
<u>3094494</u>	June 1963	Hopkins et al.	521/28	N/A
N/A				
<u>3269991</u>	August 1966	La Combe	260/79.7	N/A
N/A				
<u>3276598</u>	October 1966	Michaels et al.	210/500	N/A
N/A				
<u>3335100</u>	August 1967	Geyer	260/2.1	N/A
N/A				
<u>3419430</u>	December 1968	Michaels	736/26	N/A
N/A				
<u>3419431</u>	December 1968	Michaels	136/26	N/A
N/A				
<u>3429839</u>	February 1969	Franco	260/8	N/A
N/A				
<u>3467604</u>	September 1969	Michaels	260/2.5	N/A
N/A				
<u>3494780</u>	February 1970	Skiens	117/63	N/A
N/A				
<u>3510418</u>	May 1970	Mizutani et al.	204/296	N/A
N/A				
<u>3532527</u>	October 1970	Skiens	106/176	N/A
N/A				
<u>3544499</u>	December 1970	Hatch	260/29.6	N/A
N/A				
<u>3551331</u>	October 1967	Cescon et al.	210/321	N/A
N/A				
<u>3567632</u>	August 1969	Richter et al.	210/321	N/A
N/A				
<u>3578458</u>	May 1971	Taylor	96/115	N/A
N/A				
<u>3723386</u>	March 1973	Hatch et al.	N/A	N/A
N/A				
<u>3744642</u>	July 1973	Scala et al.	210/500	N/A
N/A				
<u>3775172</u>	November 1973	Clark	427/301	N/A
N/A				
<u>3804797</u>	April 1974	Brokterman et al.	260/29.6Z	N/A
N/A				

<u>3877978</u>	April 1975	Kremen et al.	210/23	N/A
N/A				
<u>3886066</u>	May 1975	Chen et al.	210/23	N/A
N/A				
<u>3926798</u>	December 1975	Cadotte	210/23	N/A
N/A				
<u>4005012</u>	January 1977	Wrasidlo	210/23H	N/A
N/A				
<u>4038485</u>	July 1977	Johnston et al.	422/56	N/A
N/A				
<u>4214020</u>	July 1980	Ward et al.	427/296	N/A
N/A				
<u>4277344</u>	July 1981	Cadotte	210/654	N/A
N/A				
<u>4366062</u>	December 1982	Kurihara et al.	210/651	N/A
N/A				
<u>4415455</u>	November 1983	Osei-Gyimah et al.	210/654	
N/A	N/A			
<u>4520044</u>	May 1985	Sundet	427/244	N/A
N/A				
<u>4539373</u>	September 1985	Mani et al.	525/203	N/A
N/A				
<u>4606943</u>	August 1986	Rak et al.	427/244	N/A
N/A				
<u>4634531</u>	January 1987	Nakagawa et al.	260/47R	N/A
N/A				
<u>4704324</u>	November 1987	Davis et al.	428/308.4	N/A
N/A				
<u>4705636</u>	November 1987	Small et al.	<u>210/500.42</u>	
N/A	N/A			

#### OTHER PUBLICATIONS

Schmidt, D. L., et al., J. Paint Tech., vol. 46, No. 588, pp. 41-46 (1974).

Schmidt, D. L., J. Poly. Sci., vol. 10, pp. 2951-2966 (1972).

Polymer Bulletin, 1, pp. 171-176, (1978).

ACS Symposium Series, No. 59, pp. 318-331 (1977).

Dow Chemical Company, Experimental Data.

ART-UNIT: 112

PRIMARY-EXAMINER: Niebling; John F.

ASSISTANT-EXAMINER: Gorgos; Kathryn

ATTY-AGENT-FIRM: Glenn; Michael L. Ladd; Thomas A.

ABSTRACT:

A novel composite **membrane** and methods of making the **membrane** are described. The discriminating **layer of the membrane** is prepared by reaction of a reactive cationic compound group with a compound bearing a nucleophilic moiety. At least one of the reactants bears an average of two or more reactive groups. The reaction product contains covalent bonds formed via charge eliminating reactions.

In a preferred embodiment of the invention, the nucleophilic group is anionic and a coacervate is formed initially on a microporous **substrate**. The resulting **membrane** may be useful for reverse osmosis, gas or ultrafiltration separations.

26 Claims, 0 Drawing figures

Exemplary Claim Number: 1

----- KWIC -----

Abstract Text - ABTX (1):

A novel composite **membrane** and methods of making the **membrane** are described. The discriminating **layer of the membrane** is prepared by reaction of a reactive cationic compound group with a compound bearing a nucleophilic moiety. At least one of the reactants bears an average of two or more reactive groups. The reaction product contains covalent bonds formed via charge eliminating reactions.

Abstract Text - ABTX (2):

In a preferred embodiment of the invention, the nucleophilic group is anionic and a coacervate is formed initially on a microporous **substrate**. The resulting **membrane** may be useful for reverse osmosis, gas or ultrafiltration

separations.

TITLE - TI (1):

Semi-permeable membranes prepared via reaction of cationic groups with nucleophilic groups

Brief Summary Text - BSTX (2):

Semi-permeable membranes prepared from various synthetic polymeric compositions are being used in an increasing number of commercial and industrial applications. Such uses include such diverse fields as the demineralization of saline water, gas separation, separation of organic materials, and ultrafiltration. Depending on the synthetic polymer used and the intended application, the membranes may be prepared by several methods well known to those skilled in the art. Generally such preparations include the steps of dissolving or dispersing a monomer or a prepolymer into a casting solvent, casting a film from the prepolymer, evaporating at least part of the casting solvent from the cast film, and curing the membrane. See U.S. Pat. No. 3,133,132.

Brief Summary Text - BSTX (3):

The casting solvents currently in use are mostly organic solvents such as acetone, methyl ethyl ketone, ethyl alcohol, methyl alcohol, methylene chloride, and chloroform. Such solvents are frequently costly, highly flammable or suffer from other drawbacks. Certain casting solvents present health hazards when inhaled as vapors or upon contact with the skin. The discharge of the vapors into the air also may be subject to governmental regulation necessitating some kind of recovery or disposal system. Therefore, it would be desirable to be able to cast a membrane from an aqueous mixture or solution.

Brief Summary Text - BSTX (4):

Additionally, it is important that the membrane discriminating layer be as thin as possible, while being defect free. Techniques for forming thin, uniform discriminating layers have long been sought.

Brief Summary Text - BSTX (6):

The present invention is directed to a supported, semi-permeable polymeric membrane. The supported membrane comprises at least one permselective discriminating layer affixed to a supporting surface in a manner such that when the membrane is sealingly engaged to a vessel which defines a first space communicating with a first surface of the membrane, components to which the membrane is permeable in a fluid mixture contacting the first surface of the

membrane can permeate through the membrane to a second space. Generally, the second space will not communicate with the first except by permeation through the membrane. The semi-permeable membrane has at least one discriminating layer which comprises a reaction product of a first compound bearing at least one reactive cationic moiety with a second compound including at least one nucleophilic moiety reactive with said cation group, with the proviso that at least one of the first and second compounds bears a plurality of reactive cationic or reactive nucleophilic groups or either the first or second compound is polymerizable, said reaction product containing a plurality of non-ionic bonds created with extinction of the cationic charge present in the reacting cationic group. Preferably, the reactive cationic compound is water-compatible. The first and second compounds can be the same or different and can be monomers, polymers or hydrophobes.

Brief Summary Text - BSTX (7):

As used herein, the term "water-compatible" refers to any compound which will form a stable or metastable mixture with water, including a solution, colloidal suspension, stable emulsion or dispersion, a latex and the like. "Reactive cationic moieties" and "reactive nucleophilic moieties" refer to moieties which will react with each other at conditions not deleterious to the membrane characteristics of the resulting product. The reaction of the cationic moiety with the nucleophile is one which results in the formation of covalent bonds with extinction or elimination of the cationic charge.

Brief Summary Text - BSTX (8):

The present invention also is directed to a method of forming a semi-permeable membrane. In this method, a permeable substrate bearing through physical contact or chemical bonding a plurality of reactive ionic groups of a first charge is contacted with a compound bearing at least one reactive group of a charge opposite the first charge to form an ionically-bonded, coacervate layer. The coated substrate is then subjected to conditions effective to promote reaction of a plurality of the groups ionically bonded in the coacervate layer to form covalent (i.e., essentially non-ionic) bonds. The resulting layer containing covalent bonds is essentially water insoluble (less than 0.1 percent by weight in water at 25.degree. C.).

Brief Summary Text - BSTX (9):

The invention can also be used to improve the selectivity of a semi-permeable membrane. This method comprises contacting at least one surface of the semi-permeable membrane with a first reactive aqueous ionic compound while maintaining a chemical potential gradient so as to transport water across the membrane and deposit the ionic compound on the surface of the membrane.

The surface of the membrane bearing the deposited ionic compound is then contacted with a second reactive, aqueous ionic compound of opposite charge to the deposited ionic compound, so as to form an ionically-bonded, coacervate layer. The membrane is then subjected to reactive conditions so as to convert a plurality of the ionic bonds in the coacervate layer to covalent or essentially non-ionic bonds. Preferably, sufficient covalent bonds are formed to render the discriminating layer essentially water-insoluble.

Brief Summary Text - BSTX (10):

The instant invention avoids many of the disadvantages of membranes prepared using prior art methods. Not only may the use of organic solvents be largely avoided and the entire casting procedure simplified, but certain membranes prepared using this process have demonstrated outstanding stability. This latter characteristic is highly desirable in applications where the semi-permeable membrane may be exposed to fluid mixtures containing chlorine or other oxidizers such as are frequently found in aqueous waste streams. Membranes within the scope of this invention have also demonstrated good thermal stability. Further, semi-permeable membranes within the scope of this invention have shown excellent hydrolytic (pH) stability, compaction resistance (pressure stability) and excellent selectivity and permeability in gas separations.

Brief Summary Text - BSTX (11):

Membranes within the scope of this invention include membranes used for filtration, which discriminate on the basis of size. Microfiltration and ultrafiltration membranes can be made by the practice of this invention. Particularly preferred embodiments of this invention are permselective and can be used for separation of gas components in gaseous mixtures or liquid components in fluids. Reverse osmosis, dialysis, pervaporation, gas dehydration and enrichment are all possible applications for the membranes of the subject invention. Additionally, certain of these membranes are useful in electrochemical processes or medical devices. Preferably, the discriminating layer of membranes herein described lacks sufficient ionic character to be ion selective and is not bibulous, i.e., absorbs less than about 20 weight percent water, more preferably less than about 15 weight percent water at 25.degree. C. and 100 percent relative humidity.

Brief Summary Text - BSTX (14):

The polymeric composition which constitutes the discriminating layer in the membranes of this invention results from the chemical reaction of one or more membrane precursor compounds. Typically, the discriminating layer is a water-insoluble, relatively thin, substantially continuous layer on a permeable



supporting layer.

Brief Summary Text - BSTX (15):

The membrane precursor compound or compounds are monovalent or multivalent organic radicals bearing at least one reactive moiety. This reactive moiety is either a reactive organic cation or a nucleophile, with the proviso that the cation react with the nucleophile to form nonionic bonds in the reaction product. Depending on the nature of the reactive moieties, the membrane precursor compound or compounds can be cationic, anionic, zwitterionic, amphoteric or nonionic.

Brief Summary Text - BSTX (16):

Cationic membrane precursor compounds contain reactive organic cations with the proviso that cationic moieties inert in the membrane formation reaction can also be present. Anionic membrane precursors containing anionic nucleophilic moieties can optionally bear additional anionic groups which are inert in the membrane formation reaction. Zwitterionic membrane precursor compounds bear both reactive anionic and reactive cationic moieties in equal numbers or with an excess of cationic groups. Nonionic membrane precursor compounds bear nucleophilic groups that do not bear a charge at the pH of the membrane forming process.

Brief Summary Text - BSTX (17):

The membrane precursor compounds are selected from: (1) compounds bearing hydrophobes, (2) polymerizable compounds and (3) polymers substituted with an average of more than one reactive group. Preferably, polymeric membrane precursors bear an average of at least two reactive groups.

Brief Summary Text - BSTX (18):

Hydrophobes are hydrocarbyl (i.e., a monovalent hydrocarbon radical), substituted hydrocarbyl or monovalent dialkyl siloxane groups which have low affinity for water. Operable hydrophobic groups are well known in the literature pertaining to surfactants. Illustrative hydrophobes include C.sub.8 to C.sub.20 monovalent hydrocarbon radicals, C.sub.4 to C.sub.20 perfluorinated monovalent hydrocarbon radicals or dimethyl siloxane moieties. The hydrophobe is preferably bonded to one or more reactive groups such that the membrane precursor compound forms micelles or vesicles in water.

Brief Summary Text - BSTX (19):

Polymerizable reactive cationic compounds bear one or more groups capable of reacting to form high molecular weight or crosslinked polymers in the formation of the membrane. Illustrative of such compounds are: (1) compounds with an

average of at least two reactive groups which may consist of two cationic moieties, two nucleophilic moieties or one cationic moiety together with one nucleophilic moiety; (2) compounds containing at least one reactive cationic or nucleophilic group and at least one polymerizable group such as an ethylenically-unsaturated group, a vicinal epoxide, a silanol, or the like; and (3) compounds containing reactive cationic groups which are converted into polymerizable groups during reaction of the cationic or nucleophilic group. M. J. Hatch, Progress in Organic Coatings, 1, pp. 61-78, Elsevier Sequoia S.A. (1976), describes a variety of such reactants and is incorporated herein by reference.

Brief Summary Text - BSTX (20):

Polymeric compounds include both addition and condensation polymers containing an average of more than one reactive group. The reactive moiety may be part of the polymer chain, pendant from but bonded to the chain, bonded to the ends of the chain or part of a pendant moiety bonded to the chain. The polymer can be a water-soluble polyelectrolyte or ionomer, a water-dispersible polyelectrolyte, a latex with a bound charge (see U.S. Pat. No. 4,056,501) or a water-insoluble polymer which is suitable as a support for the membrane discriminating layer.

Brief Summary Text - BSTX (22):

The molecular weight; charge density, hydrophilicity and other properties of the reactive polymers can be varied by known techniques. The optimum reactants for specific substrates, membrane formation processes and separations can then be determined empirically.

Brief Summary Text - BSTX (23):

Multi-component polymers usually consist of different monomeric units each of which contributes a desired characteristic to the resulting polymer and ultimately to the finished membrane. For example, monomers may be used which contribute nucleophilic groups for reacting with or cross-linking through the cationic group, enhance the hydrophobic or hydrophilic properties of the membrane, exert a special affinity for the species which is to be separated using the finished membrane, improve film-forming properties or adjust the mechanical properties of the resulting membrane.

Brief Summary Text - BSTX (24):

In order to impart the desired properties to the membrane discriminating layer, it is preferred that polymeric reactants can contain other groups in the repeating unit in addition to the moiety directly bearing or including the reactive cationic or nucleophilic group, provided these groups do not adversely

affect the membrane or its formation. For example, in cationic vinyl addition polymers, such methacrylate derivatives as ##STR3## wherein m is an integer from 1 to 20, may be present to advantage in membranes for reverse osmosis. For gas separation membranes and other applications where hydrolytic stability is not critical, in addition to the aforementioned methacrylate derivatives, the corresponding acrylate moieties are also operable. In addition, gas separation membranes can be derived from moieties such as ##STR4## and repeating units based on dicyclopentenyl acrylate, isobornyl acrylate, isobornyl methacrylate or dicyclopentenyl methacrylate. Isobornyl acrylate and methacrylate and dicyclopentenyl acrylate are available commercially from Alcolac, Inc.

Brief Summary Text - BSTX (27):

These reactive cationic groups must undergo a reaction which destroys or eliminates the cationic charge, e.g., nucleophilic displacement, elimination, hydrolysis, oxidation, reduction or ylid reactions, at conditions which do not deleteriously affect the desired membrane characteristics of the resulting product.

Brief Summary Text - BSTX (31):

The reactive cationic compounds can bear one or more cationic moieties with the remainder of the compound being a hydrocarbon, inertly substituted hydrocarbon, siloxane, phosphazene or other moieties compatible with the function and composition of the resulting permselective membrane. Preferably, the cationic compound does not bear any substituents or contain any covalent bonds which would be adversely affected by the conditions and compounds to which the membrane discriminating layer is subjected. Inertly-substituted hydrocarbons denotes that the remainder of the compound is not prone to deleterious side reactions.

Brief Summary Text - BSTX (32):

Preferably, the reactive cationic compounds bear an average of more than one cationic moiety per compound. Illustrative of preferred reactants are vinyl addition polymers bearing a plurality of reactive cationic moieties. The number and placement of the cationic groups in the compound can affect the membrane characteristics of the ultimate product. It is well within the skill in the art to empirically determine the cationic reactants which afford membranes of optimum characteristics in specific applications.

Brief Summary Text - BSTX (33):

The presence of hydrophobic groups and in addition to the cationic groups other hydrophilic moieties can also affect the selectivity, integrity and

permeability of the ultimate product. For example, in some preferred embodiments of this invention it is desirable that the cationic compound form thin, uniform films on a **substrate**. In such embodiments it is desirable that the cationic compound be sufficiently **hydrophobic** in character to form the desired films.

Brief Summary Text - BSTX (34):

The term reactive cationic compound as used herein refers to compounds bearing at least one cationic group. Preferably, the reactive cationic groups are substantially completely ionized in water over the entire pH range from about 2 to about 12. The cationic group preferably is covalently bonded to at least one: (a) **hydrophobic** moiety, (b) polymerizable group or (c) polymer backbone bearing a plurality of reactive cationic groups.

Brief Summary Text - BSTX (38):

The cyclic sulfonium moieties can be a 5-, 6- or 7-member ring and optionally may bear alkyl, chloro, bromo, alkoxy or other substituents which do not deleteriously affect the **membrane** formation reaction.

Brief Summary Text - BSTX (45):

A counterion (anion) will be present to balance a cationic charge. The identity of the anion is generally not critical if a coacervate is to be formed, so long as the counterion does not deleteriously affect the **membrane** to be formed. Generally, chloride, hydroxide and bicarbonate salts are preferred, with carboxylate salts being most preferred. Carboxylate, hydroxide and bicarbonate salts are preferred in coacervate formation. In some embodiments of the invention the anion can react with the cationic groups at elevated temperatures, (preferably less than 160.degree. C.), but this is not generally preferred unless the counterion is the nucleophilic reactant. The counterion is generally conveniently changed as desired by reaction with an anion exchange resin. The anion selected should not render the cationic compound water incompatible.

Brief Summary Text - BSTX (46):

A carboxylate anion is especially preferred in embodiments of the invention in which a reactive sulfonium salt is coated on a **substrate** from a solution and then dried in the essential absence of a reactive nucleophile other than the anion. The carboxylate anion is preferably the salt of a carboxylic acid which does not adversely affect the water compatibility of the cationic reactant. More preferably, the carboxylate anion is preferably a salt of a C.sub.1 to C.sub.8 carboxylic acid, a C.sub.2 to C.sub.10 dicarboxylic acid or C.sub.3 to C.sub.10 tricarboxylic acid.

#### Brief Summary Text - BSTX (49):

Not all nucleophilic groups will react with any reactive cationic compound under conditions which are not deleterious to membrane formation. The selection of a nucleophilic reactant requires consideration of: (1) the type of non-ionic bond desired in the membrane; (2) the reactivity of the cationic compound, and (3) the process and conditions employed in forming the membrane.

#### Brief Summary Text - BSTX (50):

Nucleophilic compounds useful in the subject invention can generally be selected from one of three groups: (1) nucleophilic anions of inorganic acids or water; (2) nucleophilic anions derived by removal of a labile hydrogen from organic compounds bearing such an active hydrogen, and (3) primary or secondary amines. Illustrative of the nucleophiles derived from inorganic acids or water are bromide, chloride, iodide, hydroxide, sulfite, bisulfite, phosphate, phosphite, hydrosulfide, sulfide, cyanide, cyanate and thiocyanate. Illustrative of the nucleophilic anions derived from compounds bearing active hydrogens are the conjugate bases of carboxylic acids, organic phosphonic acids, alcohols, phenols, mercaptans, thiophenols, amides, sulfonamides and phosphoric acid partial esters. Any of the foregoing nucleophilic groups can bear substituents which do not deleteriously affect the membrane or reaction by which the membrane is formed. Desirably, nucleophilic anions are selected that form adducts with one of the substituents on a heteroatom of the cationic compound, when the cation and nucleophile are present together in the presence of a solvent or diluent and the solvent or diluent is removed at a temperature less than 160.degree. C.

#### Brief Summary Text - BSTX (51):

Illustrative of the amine nucleophiles are meta-phenylene diamine, methylene dianiline, ethylene diamine, diethylene triamine and other polyamines. Compounds bearing a single amine group are operable but generally not preferred. Polymeric amines, e.g., polyethylenimine and hydrolyzed poly(ethyl-2-oxazoline), are especially preferred. Preferably, the amines are water soluble or dispersible at a slightly alkaline pH. The amine nucleophiles are especially useful for reaction with polysulfonium compounds. Amines, as well as hydrophilic inorganic nucleophiles, are particularly useful in a single coating formulation containing both cations and nucleophiles, since a coacervate will not be formed.

#### Brief Summary Text - BSTX (52):

The polymeric reactants can be derived from naturally occurring polymers, such as tannin, modified natural polymers, such as carboxymethylcellulose, or

synthetic polymers, such as acrylates. Tannic acid, for example, can be applied to a **substrate** as a colloid and then converted to its nucleophilic form by raising the pH to 7 or higher.

Brief Summary Text - BSTX (57):

The nature of the covalent bond formed in making the **membrane** depends on the specific reactants. In general for most cationic reactants, reaction with a carboxylate ion results in an ester bond, reaction with alkoxide or phenate (or other arylates) yields an ether bond and reaction with thiolate or mercaptide groups creates a sulfide bond. The reactants and process conditions should be selected to create **membranes** stable at the conditions prevailing during use of the **membrane**.

Brief Summary Text - BSTX (58):

Zwitterionic **Membrane** Precursor Compounds

Brief Summary Text - BSTX (61):

Preferred are aryl cyclic sulfonium zwitterions, e.g., ##STR25## and aliphatic cyclic sulfonium carboxylate zwitterions, e.g., ##STR26## and like compounds prepared by reaction of a sulfide with an oxirane, such as an epoxy resin. The cyclic sulfonium moieties can be a 5-, 6- or 7-member ring and optionally may bear alkyl, chloro, bromo, alkoxy or other substituents which do not deleteriously affect the **membrane** formation reaction. It has been observed that the aryl cyclic sulfonium zwitterions are generally most reactive when the sulfonium is meta relative to the anion substituent on the aryl group.

Brief Summary Text - BSTX (71):

The discriminating **layer** of the supported semi-permeable **membranes** prepared in accordance with the instant invention generally is relatively thin. Typically, the cured **membrane** excluding any porous supporting **layer** is from about 0.01 to about 10 microns thick. Preferably, the discriminating **layer of the membrane** is from about 0.05 to about 5 microns thick.

Brief Summary Text - BSTX (72):

In part because of the desired thinness of the discriminating **layer**, it is necessary to provide support to the **membrane when the membrane** is employed in a separation apparatus. In one embodiment, the peripheral area of the **membrane** is affixed to a framing structure which supports the outer edge of the **membrane**. The **membrane** can be affixed to the framing structure by a clamping mechanism, adhesive, chemical bonding or other techniques known in the prior art. The **membrane** affixed to the frame can be then be sealingly engaged in the conventional manner in a vessel so that the **membrane** surface inside the framing

support separates two otherwise non-communicating compartments in the vessel. The skilled artisan will recognize that the structure which supports the membrane can be an integral part of the vessel or even the outer edge of the membrane.

Brief Summary Text - BSTX (73):

In another embodiment of the invention, the membrane is supported on a porous substrate or structure. This porous supporting layer is characterized in that it does not significantly impede the transport across this layer of all components of a fluid in contact with the porous layer. In one preferred embodiment of the invention, the supporting layer can comprise a discriminating layer which impedes transportation of some fluid components to the membrane formed from the reactive cation and nucleophile. In another embodiment, the supporting layer can be a metal or polymeric plate with a plurality of holes or open cells. Preferably, a porous support layer possesses a high porosity as this enhances the permeability of the membrane.

Brief Summary Text - BSTX (74):

In a preferred embodiment of the invention, the porous supporting layer is a very porous polymer membrane. Illustrative of such polymeric supporting layers are microporous cellulose ester and microporous polysulfone membranes. Such membranes are commercially available under the trade names MILLIPORE, PELLICON and DIAFLO. Where such supporting membranes are thin or highly deformable, a frame may also be necessary to adequately support the semi-permeable membrane. In one especially preferred embodiment, the polymeric supporting layer is a hollow fiber of a microporous polymer such as polysulfone, polyethersulfone, polycarbonate, polybenzimidazole, cellulose acetate or other cellulose esters. The hollow fiber itself provides adequate support for the semi-permeable membrane layer coated on the inside or outside surface of the fiber. Polysulfone hollow fibers are the most preferred support for the membranes described herein.

Brief Summary Text - BSTX (75):

Methods of Making Membrane

Brief Summary Text - BSTX (76):

The reaction of the cationic and nucleophilic reactants is conducted so as to form a thin discriminating layer on a support or substrate which provides the desired mechanical strength. The reactive cationic and nucleophilic groups can be present on the same or different compounds.

Brief Summary Text - BSTX (77):

When both cationic and nucleophilic groups are attached to the same compound, the coating which reacts to form the membrane discriminating layer can be deposited on the substrate from a single coating formulation. Preferably, the compound bearing cationic and/or nucleophilic groups is water compatible, in which case an aqueous coating solution is advantageously used. Water compatible denotes that the compound is soluble or dispersible in water without formation of poorly dispersed gels, agglomerates or precipitates which are deleterious to the formation of a continuous, thin, defect-free coating on the substrate.

Brief Summary Text - BSTX (79):

Separate formulations of the reactants should also be employed when the reaction used to form the membrane is rapid. The separate formulations may be applied simultaneously or sequentially as described hereinafter.

Brief Summary Text - BSTX (82):

One important property of the coating formulation is the ability to form thin, continuous films of generally uniform thickness without defects or holes. To form such films, the coating formulation must spread readily across the surface of the substrate. For the desired spreading to occur, the spreading coefficient, i.e., the difference between the work of adhesion and the work of cohesion of the liquid, must be positive. For many water-soluble materials, surface tension increases as the solvent evaporates. Consequently, the coating formulation frequently has a tendency to draw together as it dries. The presence of small amounts of compatible organic or fluorochemical surfactants, preferably 0.05 to 0.3 percent on a solids basis by weight, alleviates this problem. Advantageously, the surfactants should be nonionic or bear charges like those of other components of the formulation. Alternatively, the cationic and/or nucleophilic reactants can include moieties which impart surface activity to the coating formulation. For example, the inclusion in a polymer of hydrophobic groups may decrease surface tension and increase viscosity of the formulation as it dries. Illustrative of such moieties is ##STR32## wherein n is an integer from 1 to 50. U.S. Pat. No. 3,965,032, in the context of linear interpolymeric interfacially spreading polyelectrolytes, describes combinations of monomers which promote film formation. These teachings are incorporated herein by reference.

Brief Summary Text - BSTX (83):

Formulations of a single or two compatible reactive compounds in a suitable diluent can be applied to the substrate by conventional coating techniques. The diluent can be any solvent or compatible diluent which does not adversely



affect the reactants, membrane support or the membrane to be formed. Conveniently, water or an aqueous diluent is employed. Small amounts of surfactants can improve the uniformity of the coating. The coating is applied to the substrate by conventional techniques, such as adsorption, dipping, casting, spraying, wiping, rolling or filtration of the coating solution through the substrate. The excess coating is desirably removed by draining or drawing a smooth instrument, e.g., a blade or roller, across the substrate surface. Where necessary, reactive compounds not compatible in a single diluent can be applied in sequential coats. Multiple coats can also be applied to eliminate defects. Multiple coats are particularly preferred in the preparation of gas separation membranes. Preferably, each coating is dried and partially cured before depositing subsequent coats. The temperature, concentration and pH of the coating solution are selected so as to avoid premature reaction and afford the desired film-forming properties. These operating parameters are generally not critical so long as the resulting membrane is not deleteriously affected. Ambient temperatures, i.e., 10.degree. to 30.degree. C. are generally convenient, although other temperatures are operable. A concentration of about 0.001 to about 5 weight percent of the reactants is preferred. The pH is selected so that the reactants are not deleteriously affected.

#### Brief Summary Text - BSTX (84):

In a preferred embodiment of the invention, separate coating formulations containing cationic reactants and anionic nucleophiles respectively are brought together on the substrate surface to form a coacervate layer at the interface. Subsequent reaction of the reactive anionic and cationic groups creates covalent bonds and a water-insensitive polymer layer. In general, water is removed and the coating heated to facilitate reaction to a water-insensitive layer. Certain highly reactive nucleophiles and cations can react in the aqueous phase. Water-insensitive denotes that the layer is not water-soluble or swollen by liquid water to a degree which adversely affects permselectivity of the layer.

#### Brief Summary Text - BSTX (85):

In sequential coating of reactive compounds, the coating of the first reactant, whether cationic or nucleophilic, is typically applied and then dried to form an adherent, uniform, comparatively thin layer on the substrate. A coating of the second reactant is then applied, advantageously washed with additional diluent and the diluent removed or coating otherwise treated to promote reaction. Advantageously, if a coacervate is to be formed, it should occur before washing the coating or removal of diluent from the second coating. This procedure can be repeated as desired in multiple coatings.

Advantageously, the ionic reactant in the first coat is a high molecular weight film-forming polymer, preferably bearing **hydrophobic** substituents to enhance its film forming properties without rendering the reactant water incompatible.

Brief Summary Text - BSTX (86):

In another embodiment of the invention, separate formulations of the cationic and nucleophilic anionic reactants are applied to opposite sides of a support that is permeable to at least one of the reactants. Preferably, a coacervate **layer** is formed at the interface where the reactants make contact. The excess formulations are then removed to leave the thin coacervate. Preferably, highly reactive combinations of the reactants and conditions which promote rapid reaction are employed to limit the thickness of the coacervate **layer**.

Brief Summary Text - BSTX (87):

The preferred reactants used in the formation of the coacervate **coatings** are separately water compatible, but together form water-insoluble, ionically-bonded adducts. In order for a coacervate to form, the reactants must bear groups with opposite charges at the pH at which the groups are in contact. In one preferred embodiment of the invention, cations present in the coacervate react via nucleophilic displacement with the nucleophilic anions present. Advantageously, covalent bond formation occurs at least in part while the coacervate **layer** is in contact with the aqueous medium. The reaction of highly reactive sulfonium ions with weakly nucleophilic carboxylate ions in an aqueous medium is relatively slow, in many instances requiring twenty-four hours or more to develop significant covalent bonding. However, this reaction rate may be practical in many applications, such as applying a discriminating **layer** on a reverse osmosis **membrane** to enhance rejection. In contrast, sulfonium groups react with thiolate ions in water at ambient temperatures to form covalent bonds in a matter of **seconds**.

Brief Summary Text - BSTX (89):

Another class of preferred reactants are polymeric, water-compatible compounds including reactive cationic polyelectrolytes, water-soluble nucleophilic polymers, water-dispersible bound charge latexes, i.e., **hydrophobic** polymer particles dispersed in water with colloiddally stabilizing ionic groups bound to the polymer, and non-ionic, water-soluble polymers and latexes bearing a plurality of primary and/or secondary amino groups. The water-soluble polymers generally will have molecular weights in the range from about 500 to about 10,000,000, preferably about 1000 to about 1,000,000. Water soluble means that the polymer is soluble to a concentration of at least 0.1 weight percent at 25.degree. C. The dispersible polymers preferably have a

mean particle diameter in the range from about 10 to about 1000 nanometers. The ionic polymers preferably have a charge density in the range from about 0.01 to about 10 milliequivalents ionic functionality per gram of polymer.

Brief Summary Text - BSTX (90):

In another preferred embodiment of the subject invention, the substrate or support itself bears reactive cationic or nucleophilic groups on at least one surface. Such substrates can be prepared by resort to a variety of techniques known in the art. Reactive monomers, such as acrylic acid or vinylpyridine, can be grafted on to the substrate and the desired nucleophile, e.g., carboxylate or cation, e.g., pyridinium, derived therefrom. The substrate can be made from a polymer or a polymer blend bearing reactive groups containing such a reactive polymer. The asymmetric microporous support can be prepared in accordance with U.S. Pat. No. 3,615,024 or other conventional techniques. Conveniently, a water-insoluble polymer is dissolved in a solvent for the polymer and a non-solvent for the polymer which is miscible with the polymer solvent is added. The non-solvent is preferably compatible with the polymer in the mixture with the polymer solvent, but is incompatible in the presence of water.

Brief Summary Text - BSTX (91):

Alternatively, the polymer substrate can be a copolymer derived from at least one monomer bearing reactive cationic or nucleophilic moieties. For example, the substrate can be a microporous copolymer of an ethylenically unsaturated monomer reacted with from about 1 to about 10 weight percent acrylic acid. Microporous substrates can be prepared in accordance with the general teachings in U.S. Pat. No. 4,020,230, which is incorporated herein by reference.

Brief Summary Text - BSTX (95):

In yet another embodiment of this invention a water-permeable membrane or substrate is coated first with a layer of an ionic polymer of a first charge to which the substrate is impermeable followed by a coating of a reactive water-compatible polymer, hydrophobe, or monomer of opposite charge to the first charge. The membrane is optionally treated in an assembled membrane device or a subassembly of a plurality of membranes which can be readily fabricated into a membrane device. In a preferred method, the feed side of the membrane is contacted with a dilute (preferably about 0.01 to about 50 parts per million (ppm) by weight) aqueous solution of a first polymeric ionic reactant while maintaining a chemical potential across the membrane, so as to transport water through the membrane. Generally, dilute solutions of 0.1 to 5 ppm by weight are preferred. Higher concentrations are operable, as long as

the viscosity is not so high as to adversely affect the membrane formation. Preferably, the chemical potential gradient is achieved by a pressure differential across the membrane, operably 0.1 to 1,500 psi, preferably about 100 to about 800 psi.

Brief Summary Text - BSTX (96):

Advantageously, the coating solution includes 50 to 5,000 ppm of NaCl or other inorganic solute, with zero to 20,000 ppm solute being operable with the proviso that the coating polymer must be compatible with the resulting solution. Preferably, contact with the first solution is maintained until either the flux through the membrane or salt rejection declines to a new steady state value. Desirably, the coating solution is circulated over the membrane surface to be treated. The feed side of the membrane is then washed with water to remove any excess of the ionic polymer. A dilute aqueous formulation of a second reactive ionic polymer or monomer opposite in charge to the first is brought into contact with the feed side of the membrane with a chemical potential applied to cause permeation of water. Once again, the chemical potential is desirably maintained until a steady state flux or salt rejection is approached. The excess of the second ionic polymer or monomer is then removed with a water wash.

Brief Summary Text - BSTX (97):

If the first reactive ionic polymer and second reactive polymer or monomer are optimally selected, they are believed to first form a coacervate and then react to form sufficient covalent bonds via nucleophilic displacement to render the product essentially water insensitive and fix it on the substrate. Advantageously, sufficient ionic bonds are converted to covalent bonds to render the discriminating layer water incompatible in a finite time.

Brief Summary Text - BSTX (98):

Preferably, the membrane treating compounds in the first formulation deposited should have a high affinity for the surface to be coated, such that they persist on the surface until affixed by formation of covalent bonds. However, compounds with low affinity for the treated surface can be used provided the chemical potential gradient is maintained until the second reactant in a two-step process has been introduced to form the coacervate. In addition to imposition of a pressure differential, other methods of producing the desired chemical potential gradient can be employed. Differences in temperature, concentration or electrical potential are also operable.

Brief Summary Text - BSTX (99):

For example, the membrane discriminating layer can be electrodeposited on a

supporting layer which is electroconductive or ion permeable. The electrodeposition technique is similar to that described in U.S. Pat. No. 3,567,613. In general, an aqueous formulation of the cationic reactant is brought in contact with the side of the support to be coated and a negative electrode disposed on the opposite side of the support. A positive electrode is placed in the aqueous coating formulation and a direct current potential sufficient to pass current is applied across the electrodes for sufficient time to deposit the cationic reactant in the desired thickness.

#### Brief Summary Text - BSTX (100):

In one preferred embodiment of the invention, a first coating of a hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA) and optionally p-nonylphenoxynonaethoxy ethyl methacrylate (9N-10MA) copolymer or terpolymer or a 95 percent vinyl acetate/5 percent crotonic acid copolymer is applied in an aqueous solution at a pH where significant carboxylate functionality is present to a substrate with an applied chemical potential. A second coating is then applied of a HEMA/VBDMS.sup.+ Cl.sup.- /9N-10MA polymer, wherein VBDMS.sup.+ Cl.sup.- is vinylbenzyl dimethyl sulfonium chloride. Preferred weight ratios of HEMA/MMA/9N-10MA in the first coating are 80:10:10 or 90:10:0. Preferred weight ratios in the second coating are 60:30:10 or 66:34:0 for HEMA/VBDMS.sup.+ Cl.sup.- /9N-10MA. Alternatively, the compositions of the nominal first and second coating can operably be applied in reverse order.

#### Brief Summary Text - BSTX (101):

In general, for reverse osmosis membranes the charge density of the first coat is advantageously not greater than the charge density of the second coat. For example, the charged moiety in the first coat whether anionic or cationic can operably constitute 10 mole percent of the polymer in the first coat and the charged moiety in the second coat can constitute 25 mole percent of this second coating material. However, significant reductions in flux were observed when the charge densities between the first and second coatings were reversed.

#### Brief Summary Text - BSTX (102):

The selection of the first and second ionic reactants and the reaction conditions will determine the characteristics of the ultimate product. The rate of formation of the coacervate may affect the membrane characteristics. Generally, coacervates which form quickly and have low water content are preferred. Additionally, the chemical stability imparted to the membrane will be influenced by the reactants. The skilled artisan can readily determine empirically the reactants and reaction conditions best suited to specific separations.

Brief Summary Text - BSTX (103):

It has been observed in treating cellulose ester reverse osmosis membranes that the cationic and anionic reactants can be applied in either order. Typically, best antifoulant behavior was achieved where the final coating was anionic. Of course, multiple sequential alternating treatments can be used in accordance with the subject method. The first and second ionic reactants are optionally each respectively mixtures of different reactive ionic groups of like charge. In one especially preferred embodiment of the invention for reverse osmosis membranes, an anionic first coat, a cationic second coat and an anionic third coat is employed.

Brief Summary Text - BSTX (104):

The membranes resulting from the aforementioned sequential treatment of permselective membranes can be used for reverse osmosis, gas separations, pervaporation or even ultrafiltration, depending upon the specific composition of the membrane. If the membrane is to be used in aqueous or liquid separations, it can be stored in the wet state after the coacervate is formed until placed in operation. If the membrane used as a substrate normally requires drying by solvent exchange, solvent extraction or freeze drying before it is used for gas separation, it should be dried by these conventional techniques after the coacervate is formed. See, for example, U.S. Pat. No. 4,430,807, which is incorporated herein by reference. Otherwise, the membrane coated with the coacervate can be dried by heating optionally at reduced pressure. The membrane generally may undergo some change in dimensions upon drying. Accordingly, if the membrane is to be dried it is desirable that the product of the cationic/nucleophilic reaction contain flexible segments which can tolerate moderate dimensional changes as occur during drying without loss of integrity. U.S. Pat. No. 3,965,032 describes moieties which impart flexibility in the context of colloiddally stable dispersions of polyelectrolytes. These teachings are incorporated herein by reference.

Brief Summary Text - BSTX (105):

The preferred membranes used as substrates for reverse osmosis are composite or asymmetric membranes having polyamide, cellulose ester or polyester discriminating layers and a salt rejection in the range from about 50 to about 99 percent using a 0.25 weight percent sodium chloride aqueous solution at 400 pounds per square inch gauge (psig). Other operable membranes useful as substrates are described in U.S. Pat. No. 4,214,020, which is incorporated herein by reference. Ultrafiltration membranes with a relatively high water flux and pore dimensions which impede passage of the first reactive coating are also preferred. More porous materials are also operable as substrates if first treated with a coating which substantially eliminates passage of liquid water

through the pores.

Brief Summary Text - BSTX (106):

In the aforementioned methods of forming membrane discriminating layers, a variety of techniques can be used to induce reactions forming covalent bonds with elimination of ionic groups. Water tends to stabilize ionic groups. Consequently, any technique that removes water from the system accelerates the elimination of ionic groups. Application of heat, radiation, certain catalysts, more reactive co-reactants or electrical potential can likewise promote the desired reactions. However, care should be taken to avoid unduly harsh reaction conditions which can promote undesirable side reactions or adversely affect the substrate or discriminating layer. Generally, the formation of covalent bonds is promoted by simultaneous moderate heating to temperatures less than 160.degree. C., preferably less than 125.degree. C., and drying. Excessive temperatures and prolonged heating are usually undesirable. In one preferred embodiment of the invention, the coating is dried, conveniently with hot air, but the supporting layer remains wet or hydrated.

Brief Summary Text - BSTX (107):

In preparing membranes according to the invention, a casting or forming solution is prepared containing a reactive cationic compound and optionally a water-soluble or water-dispersible polymer or prepolymer having free nucleophilic groups in a water-miscible solvent system usually containing water.

Brief Summary Text - BSTX (108):

In preparing composite membranes, forming solutions containing less than about 5 percent total solids are generally preferred. In forming unsupported membranes higher total solids are usually employed, the upper limit being determined by the viscosity of the casting solution.

Brief Summary Text - BSTX (109):

As already noted above, the solvent system is usually aqueous or water-dispersible. Suitable water-dispersible solvents include lower alkanols and alkylene glycols. Preferably, the forming solvent system is water-based; that is, the principal solvent is water. However, other water-dispersible or water-miscible materials may also be present in the forming solvent or the final coating formulation. Such materials may include water-miscible solvents such as lower alcohols or glycols and surfactants, extenders, or plasticizers. Such materials and their function in the forming solvent and finished membrane are well known to those skilled in the art and should require no additional

explanation.

Brief Summary Text - BSTX (110):

In carrying out the invention with certain polymers or prepolymers, such as those containing carboxylic acid groups for the active nucleophilic sites, at least part of the active groups preferably are in an ionic form, that is, in the form of a water-soluble salt. This increases the water-miscibility of the prepolymer. The particular salt is not critical to the invention so long as the cation associated with the carboxylic acid group does not interfere with the reaction between the carboxylic acid group and the reactive cationic group or adversely affect the properties of the finished membrane. Thus, ammonium salts generally have been employed and found suitable for use in this invention, but other salts such as potassium, sodium, etc., would also be satisfactory for this purpose.

Brief Summary Text - BSTX (111):

In one embodiment, a composite membrane is prepared by casting a forming solution as a uniform coating on the porous support which forms the support layer for the finished membrane. Penetration of the coating solution into micropores in the porous supporting layer and the layer itself is operable so long as the desired thickness of the semi-permeable membrane is not exceeded but is not generally preferred. Where the supporting layer is a drilled plate, a material can be placed in the drilled holes which can be readily removed or dissolved from the semi-permeable membrane. The coated membrane is dried in an oven at a temperature sufficient to remove the water of hydration. Thus, unlike casting procedures used for conventional membranes, the drying and curing of the membrane may be carried out as a single step.

Brief Summary Text - BSTX (112):

In forming unsupported membranes, the casting or forming solution can be spread on a surface from which the finished membrane may be readily separated. A convenient way of carrying out this operation is either by casting the membrane solution onto a support surface which may be dissolved away from the finished film following the drying and curing step or by casting the membrane onto a support having low surface energy, such as silicone-coated glass, or a surface to which the membrane will not adhere, such as mercury. These membranes can then be laminated on substrates, if desired.

Brief Summary Text - BSTX (113):

Membrane Compositions

Brief Summary Text - BSTX (117):



wherein a is the valence of the onium, Z.sup.+ is the onium moiety, A is a nucleophilic group or anion, X.sup.- is a compatible anion and R.sup.1 and R' are as described hereinbefore. The **second** product is the uncharged species containing the heteroatom.

Brief Summary Text - BSTX (118):

In certain preferred embodiments of the invention, R.sup.1 and R' are bonded to polymers and form part of the **membrane**. In another preferred embodiment of the invention, the substituents on the heteroatom of the onium ion together with the heteroatom form a ring structure. In the reaction with a nucleophile, an adduct is formed by elimination of one bond to the heteroatom while leaving the other bond intact. Consequently, the leaving group remains attached to the parent compound. Illustrative of such cationic reactants are the aryl cyclic sulfonium ions and the azetidinium ions. In other embodiments of the invention, either R.sup.1 --A--R' or (R.sup.1).sub.a-1 --Z can be free, mobile molecules which can be extracted from the **membrane** by volatilization or use of solvents.

Brief Summary Text - BSTX (119):

Both natural and synthetic polymers are known in the art to have permselective characteristics of potential value in making **membranes**. Only a limited number of such polymers have been used to make **membranes**. A list of some polymers evaluated previously in **membranes** is presented in D. R. Lloyd, Materials Science of Synthetic **Membranes**, pp. 64-70, ACS (1985). However, limitations in prior art techniques for fabricating **membranes** have prevented the practical realization of the permselective characteristics of many known polymers. The processes of the subject invention for making **membranes** are particularly advantageous because many polymeric materials not deleteriously affected by the subject process can be functionalized with reactive cationic and/or nucleophilic moieties. The resulting functionalized polymer can be used in the processes herein disclosed.

Brief Summary Text - BSTX (121):

The subject invention results in a variety of novel **membrane** compositions. Some of these **membranes** represent new compositions unrelated in structure to prior art **membranes**. Illustrative of novel **membrane** compositions are copolymers formed by condensation polymerization of aryl cyclic sulfonium zwitterions on the surface of a microporous **substrate**. The resulting polymer is crosslinked when a polyfunctional zwitterion is present in the reaction mixture. Copolymers of vinylidene chloride with a permeability enhancing comonomer, such as, isobornyl methacrylate and methacrylic acid, crosslinked with a bisphenol-A sulfonium zwitterion are novel. An epoxy resin modified by

reaction with a chloroacetate anion to form a carboxymethylether derivative of the formula ##STR33## can then be crosslinked by reaction with an epoxy sulfonium derivative, such as, ##STR34## Novel membrane compositions also are produced by modifying membrane forming polymers known in the prior art by incorporation of reactive nucleophilic or cationic groups and subsequent reaction by the methods of this invention to provide a novel, covalently-bonded discriminating layer. For example, poly-2,6-xylylene oxide is brominated and the bromomethyl groups thus formed are reacted with dimethyl sulfide to form a water-compatible polyelectrolyte consisting of units corresponding to ##STR35## This cationic derivative can be converted to the bicarbonate ion form by ion exchange and crosslinked via reaction with terephthalic acid.

Brief Summary Text - BSTX (124):

Polymers known in the art to have utility in membranes and bearing nucleophilic or reactive cationic groups can be crosslinked in accordance with the process of this invention with the appropriate reactant. For example, polyethylenimine can be crosslinked with bisphenol-A cyclic sulfonium zwitterion. The amine functional polymers described in U.S. Pat. Nos. 4,265,745 and 4,360,434, incorporated herein by reference, can also be crosslinked in this manner. Carboxymethyl cellulose can be crosslinked with polyvinylbenzyl dimethyl sulfonium choride. An alkali-soluble phenol formaldehyde resin can be crosslinked with a compound bearing a plurality of azetidinium groups. Hydroxyethylmethacrylate/methacrylic acid copolymer can be crosslinked with a cyclic sulfonium derivative of polyglycidyl methacrylate.

Brief Summary Text - BSTX (125):

In certain embodiments of this invention, the reactive nucleophilic or cationic compounds are intermixed with non-reactive polymerizable monomers, polymers or other compounds with desired flux and permselectivity. The reactive ionic compound present can then be crosslinked by the methods of this invention to provide novel membranes containing an interpenetrating network, a two-phase structure or other multicomponent polymer alloys, blends or composites.

Brief Summary Text - BSTX (126):

To further illustrate the subject invention, crosslinking of an aryl cyclic sulfonium moiety is preferably accomplished with almost any water-dispersible compound having an average of at least two free nucleophilic groups, such as for example a carboxyl, amino, substituted amino, amido, substituted amido, phenolic, mercapto, or alkoxide group. Illustrative compounds which the zwitterion monomers will cross-link are those prepared by addition polymerization such as, for example, a poly-N-vinyl amide, polyvinyl amine,

polyacrylate, polymethacrylate, polyacrylamide and the like. The methacrylic ester of adducts of nonylphenol and ethylene oxide are particularly preferred. Copolymers are also operable, e.g., a copolymer of vinylacetate and crotonic acid. Other suitable materials include the polymers prepared by condensation polymerization such as, for example, polyamides, modified polyesters, modified polysulfides and polybenzimidazoles or by ring opening polymerization such as, for example, branched polyethylimine and other polyaziridines and hydrolyzed polyoxazolines. Polymers derived from naturally occurring sources, such as gelatin and modified cellulose, can also be cross-linked to prepare semi-permeable membranes as described herein.

#### Brief Summary Text - BSTX (128):

In carrying out polymerization, copolymerization or crosslinking of the zwitterion monomer sufficient thermal energy should be applied to remove the water of hydration. Usually a temperature of from about 60.degree. to 160.degree. C. is sufficient to polymerize or cause crosslinking of the monomer. The resulting polymer should be crosslinked to a degree that is normally solid at the operating conditions employed for separation, but retains the desired permeability. Preferably, the semi-permeable membrane contains at least about 5 weight percent sulfonium zwitterion residue. Of course, relatively greater percentages of zwitterion are generally required to cross-link an oligomer than a polymer.

#### Brief Summary Text - BSTX (129):

Zwitterion monomers as herein described are highly soluble in water. Preferred monomers will readily form aqueous solutions in all proportions. Less water-soluble zwitterions bearing hydrophobic groups can also be used. For preparing membranes according to the present invention forming solutions may be used containing from about 0.2% to about 70% total solids by weight. Suitable solvents for the forming solution may be any solvent in which the zwitterion may be dispersed and as such includes conventional organic solvents in which the zwitterion is soluble or dispersible, so long as these are compatible with the reactants and substrate. Usually such casting solvents are water-miscible.

#### Brief Summary Text - BSTX (130):

One preferred nucleophilic prepolymer which may be used in preparing reverse osmosis membranes according to the invention may be represented by the general formula ##STR36## wherein E represents --OCH.sub.2 CH.sub.2 SO.sub.2 OG or --OCH.sub.2 CH.sub.2 OH; --G represents H, Na, K, or NH.sub.4 ; F represents --OC.sub.p H.sub.2p+1 or ##STR37## wherein p is an integer from 1 to 12, preferably from 4 to 8, and q is an integer from 1 to 50, preferably from 5 to

20; and x/y/z represents the ratio of the respective repeating units along the polymer chain. Said copolymer may be either a random, graft or a block copolymer or may be a linear or branched copolymer.

Brief Summary Text - BSTX (131):

**Membrane** devices of the spiral, tubular, hollow fiber or plate and frame configuration can also be fabricated from the novel **membranes** described herein. These devices are assembled in accordance with conventional techniques once the **membrane** is prepared. Alternatively, prior art **membranes** assembled in a device can be treated in place by the methods described hereinbefore.

Detailed Description Text - DETX (1):

The following examples will serve to further clarify the invention, but should not be construed as a limitation thereon. All percentages are by weight unless otherwise indicated. The flux and rejection of reverse osmosis **membranes** were determined at 400 psi (pounds per square inch) using 0.25 percent NaCl solution and 1 percent recovery unless otherwise indicated. The flux and rejection of reverse osmosis **membranes** were generally measured after sufficient time in operation to attain steady state values. The vinyl benzyl chloride derivatives referred to herein are 60:40 mixtures of meta and para isomers.

Detailed Description Text - DETX (4):

The casting solution was cast upon a polysulfone supporting **membrane** that had been previously washed with deionized water. The water solvent was removed from the casting solution and polymerization was effected by curing the **membrane** for 30 minutes at 110.degree. C.

Detailed Description Text - DETX (5):

Measurement of the permeation properties of this **membrane** showed an 88.5% salt rejection and an 11.0 GFD (gal/sq. ft./day) permeation rate on a 0.25% sodium chloride solution at 600 psi.

Detailed Description Text - DETX (7):

A polyethyleneimine (PEI) **coating** solution containing 2% solids was prepared by adding 12.95 g. of a 4% aqueous solution of branched PEI and 1.72 g. of a p-bisphenol A zwitterion monomer solution (28.17% solids in water) into 35.33 g. of distilled water containing the surfactant (FC-134, a cationic perfluorinated surfactant available from 3M Company under the name FLUORORAD.RTM.). The ratio of PEI to p-bisphenol A zwitterion monomer in this solution was about 52 to 48 percent by weight or 10 moles of PEI repeating units to 1 mole of zwitterion monomer. Based on total solids, the surfactant

content was about 0.1 percent by weight. The resulting solution was filtered through a 0.45 micron MILLIPORE HA-type filter.

Detailed Description Text - DETX (8):

A composite membrane was prepared using an 0.01 micron pore MILLIPORE VF-type filter as the support layer. The filter was allowed to soak in the solution prepared above for about two hours under reduced pressure. After removal from the solution, the filter was drained and placed on a clean glass plate. Additional coating solution (0.3 ml) was applied to the filter. The coated membrane was dried and cured in an air oven at 90.degree.-100.degree. C. for 35 minutes. The resulting composite membrane was stored in deionized water. Examination of the membrane using an electron microscope indicated the discriminating layer consisted of a 0.35 micron coating with some penetration of the coating material into the pores of the supporting layer.

Detailed Description Text - DETX (9):

Measurement of the permeation properties of the above membrane showed a 99.4 percent salt rejection and 0.95 GFD (gal/sq. ft./day) permeation on a 0.25 percent sodium chloride solution at 600 psig. At 710 psig, 98.4 percent salt rejection and 0.85 GFD was observed using a 1.75 percent sodium chloride solution.

Detailed Description Text - DETX (11):

Other membranes were prepared using essentially the same procedures as given in Example 2 above, except the ratio of the polymer and zwitterion was varied and other materials were used to form the support layer of the composite membrane. Permeation studies were conducted using 0.25 percent sodium chloride solution at room temperature and neutral pH. Measurements were made in a cell having either a 7.07 cm.<sup>2</sup> effective membrane area or a 39.2 cm.<sup>2</sup> effective membrane area. The results are shown in Table I.

Detailed Description Text - DETX (13):

Membranes were prepared in a manner similar to that described in Example 2 above except that the prepolymer in the coating solution was a copolymer of 2-sulfoethyl methacrylate (Na.sup.+ salt) and methacrylic acid, 90/10 by weight with M.sub.n = 149,000. The copolymer solution was 10.6 percent solids in water, pH 5.2. The monofunctional zwitterion, o-cresol zwitterion, was also used in several coating solutions. All coating solutions contained 0.1 percent (solid) surfactants (FC-128, a perfluorinated anionic surfactant available from 3M Company sold under the name FLUORORAD.RTM.). The specific results are shown in Table II.

Detailed Description Text - DETX (15):

Using the same procedures given above a composite **membrane** was prepared using a PELLICON PTHK support **layer** coated with 20 percent aqueous solution, the solids containing 32 percent by weight of a copolymer of 2-sulfoethyl methacrylate (Na.sup.+ salt) and methacrylic acid, 85 to 15 by wt. with a M.sub.n of 129,000, and 32 percent by weight o-cresol zwitterion monomer and 36 percent by weight of 1,1'-((1-methylethylidenebis(6-hydroxy-3,1-phenylene))bis(3-hydroxy tetrahydrothiophenium hydroxide)bis(inner salt). The casting solution also contained 0.1 percent FC-128 surfactant and total solids equalled 2 percent by weight. Water flux was measured at 0.5 (GFD @ 600 psi), and salt rejection was found to be 89.2 percent.

Detailed Description Text - DETX (17):

A composite **membrane** was prepared using a MILLIPORE VF filter as the support **layer**. The discriminating **layer** was cast from an aqueous **coating** mixture (2 percent total solids) containing 80 percent of a copolymer of 2-hydroxyethyl methacrylate and methacrylic acid, 90/10 by wt. with M.sub.n =21, 700, 20 percent p-bisphenol A zwitterion, and 0.2 percent FC-134 surfactant. This **membrane** had a water flux of 0.8 (GFD @ 600 psi) and a salt rejection of 96.7 percent.

Detailed Description Text - DETX (19):

A composite **membrane** was prepared using a PELLICON PTHK filter as the support **layer**. The discriminating **layer** was cast from an aqueous **coating** mixture (2.degree. percent total solids) containing 77 percent polyacrylic acid, 23 percent p-bisphenol A zwitterion, and 0.1 percent surfactant. This **membrane** had a water flux of 0.4 (GFD @600 psi) and a salt rejection of 94.8 percent.

Detailed Description Text - DETX (21):

In a similar manner, a composite **membrane** was prepared by **coating** a polysulfone support **membrane** with a casting solution (1 percent solids) containing 70 percent polyacrylamide, 30 percent p-bisphenol A zwitterion, and 0.2 percent surfactant. Water flux for this **membrane** was found to be 0.6 (GFD @ 600 psi) and salt rejection was 71.4 percent.

Detailed Description Text - DETX (23):

Using a polysulfone **membrane** as the support **layer**, a composite **membrane** was prepared from an aqueous casting solution (1 percent total solids) containing 80 percent polyethyloxazoline (46 percent hydrolyzed), 20 percent p-bisphenol A

zwitterion monomer, and 0.25 percent surfactant. This membrane had a water flux of 4.3 and a salt rejection of 36.2 percent.

Detailed Description Text - DETX (25):

In the same manner as Example 17 a composite membrane was prepared except the aqueous casting solution contained 30 percent polyacrylamido methyl propane sulfonic acid sodium salt, 70 percent p-bisphenol A zwitterion monomer, and 0.5 percent surfactant. Water flux was 0.3 (GFD @ 600 psi) and salt rejection was 54 percent.

Detailed Description Text - DETX (27):

Membranes were prepared as above except only zwitterion or an admixture of zwitterion monomers were the major film-forming components in the casting solution. Details of the membrane preparations and their desalination performance are shown in Table III.

Detailed Description Text - DETX (29):

A composite membrane was prepared using a PELLICON PTHK filter as the support layer. The discriminating layer was cast from a coating mixture (2% total solids) containing 54 percent terpolymer of methacrylic acid, 2-sulfoethyl methacrylate and methyl methacrylate (in 15/55/30 by wt.), 18 percent O-cresol zwitterion, 28 percent p-bisphenol A zwitterion and 0.5 percent surfactant. This membrane had a water flux of 1.5 (GFD @600 psi) and a salt rejection of 96.6 percent.

Detailed Description Text - DETX (31):

Three membranes prepared in a similar manner to the membrane described in Example 14 were tested for chlorine and pH stability. Membranes II and III used a cellulosic support layer and Membrane I used a polysulfone support layer. The results are shown in Table IV below.

Detailed Description Text - DETX (32):

No damage to the discriminating layer was observed as a result of exposure to the chlorine or pH extremes. Some damage to the cellulose support layer of Membranes II and III were observed at pH 11.9 which accounts for the increase in flux at the higher pH. Membrane I used a polysulfone support layer and it will be noted no increase in flux was observed at pH 11.9.

Detailed Description Text - DETX (34):

A zwitterion crosslinked polyethyleneimine composite membrane prepared as described for Example 7 was used for the separation of gases. The permeabilities of four single gases, including N.sub.2, O.sub.2, CH.sub.4 and

CO.sub.2, were measured separately through the membrane, and their relative permeabilities were calculated. The results are shown in Table V at three different humidities.

Detailed Description Text - DETX (36):

A 25 g. membrane casting solution containing 10 percent solids was formulated by mixing 22.37 g. of a poly-2-hydroxyethyl methacrylate-co-methacrylic acid (90/10 by wt.) stock solution (8.9 percent solids in water), 1.81 g. of a p-Bisphenol A zwitterion stock solution (28.1 percent solids in water) and three different perfluorinated surfactants, (all FLUORORAD.RTM. surfactants from 3M Company.). The amount of each 1% surfactant stock solution added was 0.375 g. for FC-128, 0.25 g. for FC-171 and 0.375 g. for FC-430. The ratio of polymer to zwitterion in this solution was 79.6 to 20.4 by weight or 1 to 1.1 by equivalent weight based on active functional groups. This solution was thoroughly mixed and filtered through a MILLIPORE HA-type filter with 0.45 pores and finally deaerated under a reduced pressure before uses.

Detailed Description Text - DETX (37):

Six ml of the above solution was transferred onto a silane treated glass and spread over 167 cm.sup.2 of effective membrane area. The silane coating was formed by one 5 second soak in silane agent solution (0.3 percent solids, in 10 percent isopropanol aqueous solution) and 2 hours of air drying at room temperature followed by 10 minutes heating in an air oven at 100.degree. C. The silane-treated glass plate was then framed with two layers of masking tape to form a shallow trough to contain the membrane solution.

Detailed Description Text - DETX (38):

Water in the membrane solution was allowed to evaporate slowly at room temperature overnight and then further removed by drying the glass plate supported membrane in a vacuum oven at 25.degree.-35.degree. C. for 7 days. Finally, the membrane was insolubilized by curing in an air oven at 90.degree. C. for 20 minutes, then at 120.degree. C. for 40 minutes.

Detailed Description Text - DETX (39):

The insolubilized zwitterion membrane was removed from the glass plate by a sequential swelling treatment:

Detailed Description Text - DETX (43):

The membrane was then washed with a large amount of D.I. water and finally soaked in a diluted pH 7 buffer solution.



Detailed Description Text - DETX (44):

This membrane exhibited a 94.2 percent salt rejection to a 0.25 percent NaCl solution and a 0.1 GFD of water flux under 600 psi applied pressure.

Detailed Description Text - DETX (45):

EXAMPLE 27 A 35 g. coating solution containing 2% solids was formulated by adding 0.344 g. of a branched polyethylenimine dry sample and 1.202 g. of a p-Bisphenol A zwitterion stock solution (29.6 percent solids in n-butanol), together with 33.45 g. of n-butanol (reagent grade). The water contents in the p-Bisphenol A zwitterion stock solution and the formulated coating solution measured by Fisher titration were 0.077 and 0.613 percent by weight, respectively. This coating solution was filtered through a double layered, MILLIPORE LS-type TEFLON filter.

Detailed Description Text - DETX (46):

A PELLICON PTHK-type ultrafilter was selected as a porous substrate for making a composite membrane from the filtered coating solution.

Detailed Description Text - DETX (47):

The resulting membrane exhibited a 93.2 percent salt rejection to a 0.25 percent sodium chloride solution and a water flux of 5.8 GFD at 600 psi applied pressure.

Detailed Description Text - DETX (49):

A terpolymer prepared by the addition polymerization of 80 parts 2-hydroxyethyl methacrylate, 10 parts methacrylic acid and 10 parts of a methacrylate ester of an adduct of nonylphenol and a polyethylene glycol containing 10 equivalents of ethylene oxide was employed as a component of a membrane casting solution. All parts and percentages are by weight. This casting solution contained 2 percent solids consisting of 78.2 percent of the terpolymer, 21.8 percent of a p-Bisphenol zwitterion and 0.3 percent of a perfluorinated surfactant (sold under the trademark FC-128 by 3M Company) and 98 percent water.

Detailed Description Text - DETX (50):

A PELLICON PTHK filter was coated with an excess of the membrane casting solution, drained rapidly and then heated with a heating lamp until ostensibly dry. The filter was then cured in air at 120.degree. C. for 40 minutes.

Detailed Description Text - DETX (51):

The resulting composite membrane exhibited 98.4 percent salt rejection and 0.07 GFD water flux when subjected to a 0.25 percent aqueous NaCl solution at

600 psi applied pressure.

Detailed Description Text - DETX (53):

A polyvinyl acetate/crotonic acid copolymer sold by Monsanto under the tradename Gelva (Grade C-5V-16M) was employed as a component in a membrane casting solution. The copolymer was used in the ammonium salt form in a 10 weight percent solids solution in water having a pH of 9.3. To 8.52 grams of the copolymer solution was added 0.528 gram of a p-Bisphenol A zwitterion monomeric aqueous solution containing 28.1 percent solids, 0.3 gram of 1 weight percent of a perfluorinated surfactant in a 10 weight percent isopropanol, 90 weight percent water solution (under the trademark FC-128 sold by 3M Company) and sufficient deionized water to make a solution totalling 50 grams. In this solution there is approximately 1.5 equivalents of zwitterion monomer for each equivalent of carboxylic acid present.

Detailed Description Text - DETX (54):

The casting solution was filtered and then a PELLICON PTHK filter was soaked in the solution for 2 hours. The filter was drained for 30 seconds while held in a vertical orientation and then 0.1 milliliter of additional casting solution was distributed uniformly over the filter. The filter was dried in air for 2 hours at 20.degree. C. and then cured at 115.degree. C. for 45 minutes.

Detailed Description Text - DETX (55):

The resulting composite membrane exhibited 99.4 percent salt rejection and 0.05 GFD water flux at 40.degree. C. when contacted with a 0.24 weight percent aqueous NaCl solution at 600 psi applied pressure.

Detailed Description Text - DETX (57):

A membrane casting solution containing 3 weight percent solids consisting of 22.5 weight percent of dimethyl malonic acid in ammonium salt form and 77.5 weight percent p-Bisphenol A zwitterion monomer and 0.5 weight percent of a surfactant (sold under the tradename Triton X-100) was liberally coated on a PELLICON PTHK filter. The filter was drained briefly, placed in a framing support and dried in a microwave for 3 minutes. The filter was then cured in air at 125.degree. C. for 30 minutes.

Detailed Description Text - DETX (58):

The resulting composite membrane exhibited 87.6 percent salt rejection and 0.005 GFD water flux at 40.degree. C. when contacted with a 0.25 weight percent aqueous NaCl solution at 600 psi.

Detailed Description Text - DETX (61):

Composite **membranes** were prepared using a Millipore VSWP-type filter as a support **layer**. The filter was secured at a top edge and disposed so the top side makes about a 135.degree. angle from horizontal. An aqueous solution of an anionic polymer at a solids concentration of 2 weight percent was applied uniformly to the top of the filter and allowed to flow so as to wet the filter surface uniformly. The **coating** solution also contained 0.2 weight percent of a perfluorinated surfactant (FC-128) and from 7 to 20 percent of a zwitterion corresponding to Structure 1 in Table VI as a crosslinker.

Detailed Description Text - DETX (63):

After the aqueous anionic polymer had contacted the filter for ten **seconds**, the excess solution was removed by blotting the filter at the lower edge with absorbent paper. The **coating** was then cured at 85.degree. C. for 15 minutes. The filter was rotated 180.degree. C. in the same plane. The anionic coated filter was then coated a **second** time in the same manner except a 1 percent solids anionic polymer solution was employed. In Examples 58 and 59 and Comparative Experiments 26 and 27 a 0.5 percent solids solution was used. The coated filter was then cured at 85.degree. C. for 15 minutes, except in Example 33 which was cured at 100.degree. C. for 15 minutes.

Detailed Description Text - DETX (66):

Both the control filters and filters coated with an anionic base coat and cationic wash were immersed in water for about 2 to 12 hours and cut to fit a reverse osmosis test cell. The salt rejection and water flux was determined using a 0.25 percent NaCl solution at 400 psi with a flow rate of 55 to 65 milliliters per minute. The **coating** parameters, including the cation structure from Table VI, the cation concentration in weight percent, cure temperature in .degree.C. and cure time in minutes for cationic **coating** and the identity of the anionic polymer and percent zwitterion present in the anionic **coating** and test results are tabulated in Table VII.

Detailed Description Text - DETX (69):

Four filters were coated with a 2 weight percent aqueous anionic polymer solution in the general manner of Example 31. The anionic polymer was 93 weight percent Polymer B as in Example 56 and included 7 weight percent of the zwitterion of Structure 1 in Table 6. The anionic **coating** solution also included 0.2 weight percent FC-134 surfactant on a solids basis. After curing the first coat at 85.degree. C. for 15 minutes the **coating** process was repeated using a 1 weight percent solution. The coated filters were then immersed in water for 2 hours.

Detailed Description Text - DETX (71):

The treated filters and two controls were tested for salt rejection and flux as in Example 31. The results are tabulated in Table VIII. It is believed that some decomposition of the diazonium between the first and second filters treated accounts for the lower rejection obtained with the second sample.

Detailed Description Text - DETX (73):

Twenty grams of a 2 weight percent aqueous solution of a cationic reactant were mixed with twenty grams of a 2 weight percent aqueous solution of a vinyl addition polymer prepared from methyl methacrylate and ##STR52## in a mole ratio of 70:30. To the aqueous mixture was added 0.2 percent on a solids basis FC-134 surfactant. The resulting solution was used to coat two filters in the manner of Example 31 and the coating cured at 85.degree. C. for 2 hours. The identity of the cationic reactant and flux and salt rejection when tested as in Example 31 are tabulated in Table IX.

Detailed Description Text - DETX (90):

A microporous polysulfone sheet (sold commercially as Millipore Pellicon PTHK membrane) was washed with deionized water and dried.

Detailed Description Text - DETX (92):

The polymers prepared in Examples 74-76 and others made in an analogous manner were reacted with an anion exchange resin to replace the chloride anions present with hydroxide anions. The resulting polymers were prepared as 2 percent aqueous solutions with a pH in the range from 10.8 to 12.85. To each solution was added 0.2 or 0.3 percent of FLUORAD.RTM. FC-134 cationic surfactant (based on the solids present). Each of these solutions was used to coat on side of the aforementioned coated polysulfone. The sheets were then cured at 110.degree. C. for 20 or 25 minutes. The resulting membrane was soaked overnight in deionized water. A 1.2-square inch membrane section was cut out for testing in each instance. Frequently, multiple membranes of the same composition was prepared.

Detailed Description Text - DETX (93):

The percent salt rejection and water flux were measured for each membrane using an aqueous test solution containing 2500 ppm NaCl at 25.degree. C. and a pH of 7 at an operating pressure of 400 or 600 psi with a recovery of less than 1 percent. The composition of the top coat (before conversion to hydroxide form), the pH of the top coat solution, the operating pressure, water flux and salt rejection are tabulated in Table II.

Detailed Description Text - DETX (95):

Twice-coated polysulfone membranes were prepared in the manner of Examples 79, 81, 83 and 87 except that the HEMA/9N-10MA/MAA prime coat was employed at a concentration of 1.5 percent and was dried for 8 minutes at 110.degree. C. The composition of the top coat and the flux and salt rejection at 400 psi are tabulated in Table XIII.

Detailed Description Text - DETX (98):

Twice-coated polysulfone membranes were prepared in the manner of Example 89, except that the prime coat was employed at a concentration of 0.75 or 0.3 percent. The prime coat concentration as well as the flux and salt rejection at 400 psi are tabulated in Table XIV.

Detailed Description Text - DETX (99):

Examples 89 and 96-99 demonstrate that the concentration of the prime coat can affect the uniformity of the coating laid down on the substrate.

Detailed Description Text - DETX (101):

A microporous cellulose ester sheet available commercially under the tradename Millipore VS-type filter was employed as the substrate. The HEMA/9N-10MA/MAA terpolymer prepared in Example 79 was converted to its ammonium form and diluted to a concentration of 0.3, 0.75 or 1.5 percent. To each solution was added 0.3 percent (based on solids present) of FLUORAD.RTM. FC-128 surfactant. The substrate was immersed in these solutions for one hour under reduced pressure, drained for one minute and then dried at 110.degree. C. for 10 minutes.

Detailed Description Text - DETX (102):

The coated substrates were then top-coated on one side in the same manner and with the same solution as in Example 83 and cured at 110.degree. C. for 20 minutes. The prime coat concentration and the flux and salt rejection of the membranes at three pressures using a 2500 ppm NaCl aqueous solution at less than 1 percent recovery are set out in Table XV.

Detailed Description Text - DETX (104):

The membranes employed in Examples 81-84 were employed in chlorine stability tests. These membranes were employed with a 2500 ppm NaCl aqueous feed at 400 psi and 25.degree. C. and less than 1 percent recovery. For the first 775 hours of the test the feed water was at a pH of 4.5 and contained 10 ppm Cl.sub.2. The membranes were then operated for 72 hours with distilled water. The 10 ppm Cl.sub.2 feed was resumed for 96 hours at pH 4.5 followed by 156 hours at pH 8.0. The flux in GFD and percent salt rejection for each membrane are tabulated in Table XVI.

Detailed Description Text - DETX (105):

Examples 103-106 demonstrate that these performance membranes exhibit superior chlorine tolerance.

Detailed Description Text - DETX (107):

In a manner generally similar to Example 73, HEMA, VBDMS.sup.+ Cl.sup.-, 9N-10MA and MAA were polymerized in a ratio of 49.5:30.5:8.0:12.0. The polymer was then passed through a column of DOWEX.RTM. SBR ion exchange resin in hydroxide form to convert the polymer to a zwitterion. A 2 percent solution of the resulting polymer in water along with 0.2 percent on a solids basis FLUORAD.RTM. FC-134 surfactant was coated on a Millipore VS-type cellulose ester filter and cured at 100.degree. C. for 30 minutes. The resulting membrane had a salt rejection of 97% and a flux of 0.6 GFD using a 2500 ppm NaCl feed at 400 psi.

Detailed Description Text - DETX (110):

The aqueous polymer solution was coated using a coating roll on a flat, wettable, microporous polysulfone sheet manufactured by FilmTec Corp. The coated sheet was air-dried at 110.degree. C. in an oven for about 25 minutes. Three samples of the resulting composite membrane had a salt rejection in the range from 96.4 to 98.4 percent and a flux in the range from 2.5 to 3.8 GFD using a 2500 ppm NaCl feed at 400 psi.

Detailed Description Text - DETX (113):

The aqueous polymer solution was coated using a coating roll on a flat, wettable, microporous polysulfone sheet. The coated sheet was air-dried at 110.degree. C. for about 25 minutes. Three samples of the resulting composite membrane exhibited salt rejections in the range from 96.3 to 97.7 percent and fluxes in the range from 2.7 to 3.6 GFD using a 2500 ppm NaCl feed at 400 psi.

Detailed Description Text - DETX (115):

In a manner generally similar to Example 76, a polymer of HEMA, VBDMS.sup.+ Cl.sup.- and 9N-10MA in a weight ratio of 50:40:10 was prepared. A microporous cellulosic filter (Example 110) was coated on one side with a 1 percent aqueous solution of polyacrylic acid (PAA) in the ammonium salt form. A second filter (Example 111) was coated on one side with a 2 percent aqueous solution of branched polyethyleneimine (PEI). Both coated filters were coated on the other side with the aqueous HEMA/VBDMS.sup.+ OH.sup.- /9N-10MA and surfactant formulation of Example 108 and cured at 110.degree. C. for 25 minutes.

Detailed Description Text - DETX (117):

A microporous polysulfone filter (Example 113) was coated with a 1 percent aqueous solution of HEMA/VBDMS.sup.+ Cl.sup.- /9N-10MA polymer as in Example 76

and ammonium citrate in a 1:1 equivalent weight ratio. The **coating** solution included 0.3 percent FC-128 surfactant on a solids basis. The coated filter was then cured at 110.degree. C. for 25 minutes.

Detailed Description Text - DETX (118):

A microporous polysulfone filter (Example 114) was coated with a 1 percent aqueous solution of HEMA/VBDMS.sup.+ Cl.sup.- /9N-10MA polymer as in Example 76

and branched polyethyleneimine in a 1:2 equivalent weight ratio. The **coating** solution included 0.3 percent FC-134 surfactant on a solids basis. The coated filter was cured at 110.degree. C. for 25 minutes.

Detailed Description Text - DETX (119):

The rejection and flux of the aforementioned coated **membranes** using a 0.25 percent NaCl solution at 400 psi is tabulated in Table XVII.

Detailed Description Text - DETX (130):

A microporous cellulosic filter was soaked for 2 hours in a 0.56 percent solution of HEMA/9N-10MA/methacrylic acid terpolymer in a 80/10/10 weight ratio and 0.3 percent FC-128 surfactant on a solids basis. The **coating** solution had a pH of 9.1 and salts present were in the ammonium form. The filter was then drained and dried on a glass plate at 100.degree. C. for 6 minutes. The coated filter was then cooled to about 20.degree. C. and recoated. Excess solution was removed by rolling a No. 8 wire **coating** rod over the surface. The twice coated filter was then dried once more at 100.degree. C. for six minutes.

Detailed Description Text - DETX (131):

A **second coating** solution containing 2 percent VBDMS.sup.+ OH.sup.- homopolymer and 0.3 percent on a solids basis of FC-134 surfactant was prepared. The **coating** solution was applied to coated filter and excess removed with a **coating** wire. The filter was then dried at 100.degree. C. for 10 minutes. The **coating** and drying steps were repeated twice more with the last drying step being extended to 20 minutes.

Detailed Description Text - DETX (132):

The resulting **membrane** was soaked in 3.5 percent aqueous NaCl overnight. A sample of the **membrane** was then cleaned in deionized water and dried in air at room temperature: Gas permeation rates (cm.sup.3 (STP)/(cm.sup.2 /sec/cm-Hg)

for oxygen, nitrogen, carbon dioxide and methane were determined and are tabulated in Table XIX.

Detailed Description Text - DETX (136):

A small piece of the coated fabric was tested at standard reverse osmosis conditions for both flux and rejection in a comparative experiment. The membrane was then treated with 25 ppm VBDMS.sup.+ OH.sup.- homopolymer at 400 psi. The feed flow rate was adjusted to consume 0.5 liter solution in a 3 hour period. The membrane was washed with water and flux and rejection measured. The reverse osmosis performance is tabulated in Table XX.

Detailed Description Text - DETX (138):

Reverse osmosis membranes and controls were prepared in the general manner of Example 31. The cationic reactant corresponds to structure 12 in Table VI. The flux and rejection are tabulated in Table VII for these membranes.

Detailed Description Text - DETX (140):

A Millipore VS filter with a nominal pore size of 0.025 microns was coated with a 2 percent solids aqueous solution. The solids in the solution consisted of 80 weight percent polyacrylamide (of which 5.5 percent was hydrolyzed) and 20 weight percent of p-bisphenol-A sulfonium zwitterion. In addition, the solution contained 0.25 percent FC134 surfactant on a solids basis. The coating was cured at 87.degree. C. for 1 hour.

Detailed Description Text - DETX (141):

The coated filter was used to filter a 5 percent glucose solution at 10 psi. The flux was 0.3 milliliter per minute (ml/min) and the rejection was 40 percent. A solution containing 5 percent sucrose was filtered at 10 psi, with a flux of 0.1 ml/min and rejection of 100 percent. Accordingly, the membrane has a molecular weight cut-off of about 300.

Detailed Description Text - DETX (143):

Millipore ultrafiltration filters of type VSWP having a nominal pore diameter of 0.025 microns were coated with an aqueous solution containing 2 weight percent solids. The solids consist of 29.3 percent by weight bisphenol-A sulfonium zwitterion and 68.5 percent of a t-butyl monophenol sulfonium zwitterion corresponding to the formula ##STR56## Additionally 0.2 percent on a solid basis of FC134 surfactant is present and 2 percent on a solids basis NATROSOL.RTM. 250HR thickener from Hercules. The coating was dried between applications of coats at 85.degree. C. for 5 minutes. Four coats were applied in all. The final coat was cured at 85.degree. C. for 60 minutes.



Detailed Description Text - DETX (144):

The gas permeability of four membrane samples was measured for oxygen, nitrogen, carbon dioxide and methane at pressure differentials of either 15 or 2 psi at a temperature of 23.degree. C. The permeabilities are tabulated in Table XXI.

Detailed Description Text - DETX (146):

A crosslinked membrane is prepared by casting a film from a solution of 1.36 grams of sodium carboxymethylcellulose, (carboxymethyl degree of substitution=0.9); 0.34 grams of sodium polyacrylate (5000 molecular weight); 0.09 grams of a bisphenol-A sulfonium zwitterion; 2 grams of a 1 weight percent surfactant solution and 38.2 grams of water. The film is cast onto a fluorinated hydrocarbon polymer surface using a 0.025 inch casting knife. The film is dried overnight and then heated to 110.degree. C. for 1.5 hours to induce crosslinking. The resulting membrane is water-insoluble. The membrane is evaluated using an initial feed mixture of ethanol/water containing about 51 weight percent water until the water content of the feed is reduced to 39.37 percent. The water contents of the feeds and permeates, separation factors and the permeation rates for this example are as recorded in Table XXII.

Detailed Description Text - DETX (147):

The feed is then replaced with a 10.5 percent water, 89.5 percent ethanol solution and the membrane is again evaluated. After the feed composition reaches 10.33 percent water, 2 grams of 50 percent solution of cesium hydroxide is added to the feed and the membrane is allowed to equilibrate overnight. The membrane is then further evaluated with results as shown in Table XXIII.

Detailed Description Text - DETX (148):

The crosslinked membranes of this invention exhibit excellent selectivity, as shown by the permeate composition, even at very high feed water content and very high permeation rates. Moreover, the membrane exhibits no signs of failure despite the high water content in the feed. Upon reducing the water of the feed to about 10 percent, the permeation rate decreases dramatically and the permeate composition increases to over 99 percent water. It is noted that the addition of the cesium to the feed results in a tripling of the permeation rate with only a minimal decrease in the water content of the permeate. Even when using cesium as the counterion, the permeate consistently contains at least 99.6 percent water.

Detailed Description Text - DETX (150):

Cellulose triacetate (CTA) hollow fiber membranes were sequentially treated

at 200 psi and 20.degree. C. with (1) an aqueous solution of 25 ppm of a copolymer of 95 weight percent vinyl acetate and 5 weight percent crotonic acid at a pH of 7.5 at a flow rate of 120 ml/min for 3 hours followed by (2) an aqueous solution of 25 ppm of a terpolymer of HEMA/VBDMS.sup.+ Cl/9N10MA (as in

Example 92) in a ratio of 60:30:10 by weight at a flow rate of 2.5 grams per minute for three hours. In between the two aqueous solutions, the fibers were flushed with water.

#### Detailed Description Text - DETX (151):

After coating the external surface of the fibers, a 50:50 volume mix of isopropanol and isooctane was passed through the fiber bores at 15 psig while air was passed over the external fiber surface to dry the fibers in the manner of U.S. Pat. No. 4,430,807, which is incorporated herein by reference. After several hours, nitrogen was introduced into the fiber bores while first air was passed over the external surface and then a vacuum applied to complete drying.

#### Detailed Description Text - DETX (152):

The dry CTA membranes were prepared in the aforementioned manner and tested to determine permeability to carbon dioxide and methane. The coated membrane exhibited 30 percent lower flux for carbon dioxide but a 19 percent higher separation factor than otherwise similar uncoated membranes.

#### Detailed Description Paragraph Table - DETL (1):

TABLE 1

---

Composition of	<u>Coating</u>	Solution	Desalination	(wt. %)	Performance	Example
p-bisphenol	Type of Water	Salt	Number	PEI	A Zwitterion	Surfactant Porous
Support	Flux*	Rejection (%)				

---

	3	52				
48 -- Polysulfone	1.9	98.6	4	44	56	0.1 PELLICON PTHK 0.2 99.8 5 55 45 0.1 "
1.0 99.7	6	72	28	0.1	"	3.5 98.2 7 55 45 0.1 MILLIPORE VS 0.6 99.7

---

\*GFD  
at 600 PSI.

#### Detailed Description Paragraph Table - DETL (2):

TABLE II

Composition of **Coating** Solution Desalination (wt. %) Performance Example  
 p-bisphenol o-cresol Type of Water Salt Number Prepolymer A Zwitterion  
 Zwitterion Porous Support Flux\* Rejection (%)

---

8 40  
 24 36 Polysulfone 1.7 97.5 9 40 24 36 " 1.7 96.2 10 40 24 36 MILLIPORE VS  
 21.3 63.6 11 40 24 36 MILLIPORE VF 4.8 84.2 12 56 44 -- Polysulfone 1.3  
 98.5

---

\*GFD  
 at 600 PSI.

Detailed Description Paragraph Table - DETL (3):  
 TABLE III

---

Desalination Composition of **Coating** Solution Performance Example (wt. %)  
 Solid Water Salt Number OCZ.sup.1 HEPZ.sup.2 PBAZ.sup.3 HTBA.sup.4  
 Surfactant Content Flux.sup.5 Rejection (%)

---

19  
 60 40 0.1 1 0.04 64.9 20 100 0.2 3 0.1 28.5 21 100 0.2 3 0.6 10 22 83 17  
 0.2 3 0.15 33

---

.sup.1 OCZ = o-cresol zwitterion. .sup.2 HEPZ = o-hydroxyethoxy phenol  
 zwitterion. .sup.3 PBAZ = p-bisphenol A zwitterion. .sup.4 HTBA =  
 1,1((1-methylethylidene  
 bis(6-hydroxy-3,1-phenylene)bis(3-hydroxytetrahydrothiophenium hydroxide) bis  
 (inner salt). .sup.5 GFD at 600 psi.

Detailed Description Paragraph Table - DETL (4):  
 TABLE IV

---

**Membrane I** **Membrane II** **Membrane III** Water Salt Water Salt Water Salt Test  
 Conditions Flux\* Rejection (%) Flux\* Rejection (%) Flux\* Rejection (%)

---

(1)  
 After 70 hours 0.27 89.6 0.45 96.8 0.45 94.3 (2) 3-5 ppm Cl 0.23 86.2  
 0.45 97.4 0.46 94.3 pH 6-7 After 90 hours (3) pH 11.9 0.29 82.8 1.5 91.5  
 1.5 90.2 After 26 hours (4) After 24 hours 0.30 88.7 1.7 96.9 1.7 96.7

---

\*GFD  
at 600 PSI.

Detailed Description Paragraph Table - DETL (5):  
TABLE V

---

(Flow Rate of Feed Gas = 5-20 cc/sec) Measured at Room Temperature Humidity  
Applied Contents Pressure Gas Permeability (cc(std)/cm.<sup>2</sup>/sec/psi)  
Relative Permeability In Feed Gases (psi) O.<sub>2</sub> N.<sub>2</sub> CH.<sub>4</sub>  
CO.<sub>2</sub> O.<sub>2</sub> N.<sub>2</sub> CH.<sub>4</sub> CO.<sub>2</sub> CO.<sub>2</sub>/CH.<sub>4</sub>

---

For  
**Membrane** (Desalting Ability: 98.4% Rejection; 0.8 GFD @ 600 psi) (1)  
Dry.<sup>(1)</sup> 100 3.83 .times. 10.<sup>-6</sup> 4.64 .times. 10.<sup>-6</sup> 6.74 .times.  
10.<sup>-6</sup> 4.93 .times. 10.<sup>-6</sup> 1 1.2 1.8 1.3 0.73 150 4.41 .times.  
10.<sup>-6</sup> 5.28 .times. 10.<sup>-6</sup> 8.05 .times. 10.<sup>-6</sup> 5.39 .times.  
10.<sup>-6</sup> 1 1.2 1.8 1.2 0.67 200 4.96 .times. 10.<sup>-6</sup> 6.17 .times.  
10.<sup>-6</sup> 8.92 .times. 10.<sup>-6</sup> 6.31 .times. 10.<sup>-6</sup> 1 1.2 1.8 1.3  
0.71 (2) 93% RH.<sup>(1)</sup> 100 3.67 .times. 10.<sup>-6</sup> 1.34 .times. 10.<sup>-6</sup>  
5.06 .times. 10.<sup>-6</sup> 1.72 .times. 10.<sup>-5</sup> 1 0.37 1.4 4.7 3.4 150 4.26  
.times. 10.<sup>-6</sup> 3.83 .times. 10.<sup>-6</sup> 6.09 .times. 10.<sup>-6</sup> 1.75 .times.  
10.<sup>-5</sup> 1 0.90 1.4 4.1 2.9 200 4.85 .times. 10.<sup>-6</sup> 4.71 .times.  
10.<sup>-6</sup> 7.18 .times. 10.<sup>-6</sup> 1.64 .times. 10.<sup>-5</sup> 1 0.97 1.5 3.4  
2.3 (3) 100% RH.<sup>(2)</sup> 100 2.63 .times. 10.<sup>-7</sup> 1.0 .times. 10.<sup>-7</sup>  
2.02 .times. 10.<sup>-7</sup> 4.02 .times. 10.<sup>-6</sup> 1 0.38 0.77 15. 20. 150  
2.38 .times. 10.<sup>-7</sup> 1.13 .times. 10.<sup>-7</sup> 2.10 .times. 10.<sup>-7</sup> 5.20  
.times. 10.<sup>-6</sup> 1 0.47 0.88 22. 25. 200 2.72 .times. 10.<sup>-7</sup> 1.23  
.times. 10.<sup>-7</sup> 1.75 .times. 10.<sup>-7</sup> 6.31 .times. 10.<sup>-6</sup> 1 0.45 0.64  
23. 36.

---

NOTES: .<sup>(1)</sup> **Membrane** was dried (25-35.degree. C., high vacuum; 48 hours)  
before conducting measurements with dry feed gases and 93% relative humidity  
feed gases formed by feed gases through a saturated Na.<sub>2</sub> SO.<sub>4</sub>  
solution. .<sup>(2)</sup> **Membrane** was flooded with D.I. water at low pressure (20  
psi) prior to gas permeation measurement. Feed gases were bubbled through D.I.  
water before entering test cell.

Detailed Description Paragraph Table - DETL (10):  
TABLE X

Rejection Example

## Coating

Time Flux (GFD) (%) \_\_\_\_\_ 69 4 hours 0.392  
82.11 70 2 hours 0.281 88.51 71 10 minutes 0.575 82.16

---

### Detailed Description Paragraph Table - DETL (16): TABLE XVI

---

Example 103.sup.a Example 104.sup.b Example 105.sup.c Example 106.sup.d  
Flux Rejection Flux Rejection Flux Rejection Flux Rejection Operating  
Conditions (GFD) (%) (GFD) (%) (GFD) (%) (GFD) (%)

---

10  
ppm Cl.sub.2 at pH 4.5 After 7 hours 1.33 90.2 0.37 96.4 0.77 91.5 0.29  
96.6 After 100 hours 1.40 93.8 0.37 96.4 0.81 93.9 0.30 96.7 After 300  
hours 1.42 93.5 0.38 96.1 0.78 93.1 0.31 95.0 After 500 hours 1.42 93.1  
0.40 96.4 0.85 92.3 0.33 95.1 After 775 hours 1.24 91.5 0.36 95.2 0.74  
87.8 0.30 92.9 Water Feed 1.56 -- 0.44 -- 0.89 -- 0.34 -- 10 ppm Cl.sub.2  
at pH 4.5 After 18 hours 1.20 87.8 0.36 93.3 0.68 85.4 0.29 92.4 After  
96 hours 1.33 92.1 0.39 94.1 0.77 90.1 0.31 93.9 10 ppm Cl.sub.2 at pH  
8.0 After 37 hours 1.56 69.8 0.44 85.9 0.90 69.4 0.36 88.9 After 156  
hours 1.66 70.2 0.44 89.7 0.67 68.9 0.36 88.3

---

.sup.a **Membrane** used in Example 81. .sup.b **Membrane** used in Example 82.  
.sup.c **Membrane** used in Example 83. .sup.d **Membrane** used in Example 84.

#### Claims Text - CLTX (1):

1. Method of improving the selectivity of a semi-permeable **membrane** comprising:

#### Claims Text - CLTX (2):

(a) contacting the **membrane** with a first reactive, ionic compound in an aqueous diluent while maintaining chemical potential gradient so as to deposit the ionic compound on **membrane** surface; and

#### Claims Text - CLTX (3):

(b) maintaining chemical potential gradient while contacting the **membrane** in an aqueous diluent with a **second** reactive, ionic compound of a charge opposite to the first compound, so as to form a coacervate.

Claims Text - CLTX (4):

2. The method as described in claim 1 further comprising subjecting the **membrane** to reactive conditions so as to convert a plurality of ionic bonds in the coacervate **layer** to covalent bonds.

Claims Text - CLTX (5):

3. The method as described in claim 2 wherein the chemical potential gradient is due to a pressure differential applied across the semi-permeable **membrane** which results in water being transported through the **membrane**.

Claims Text - CLTX (6):

4. The method as described in claim 2 wherein the coacervate forming compounds are deposited on the semipermeable **membrane** by an electrical gradient maintained across the semipermeable **membrane** in an aqueous solution.

Claims Text - CLTX (7):

5. The method as described in claim 2 wherein either the first or **second** reactive compound bears a plurality of ionic groups selected from the group consisting of sulfonium, quaternary ammonium, phosphonium, pyridinium, thiazolinium, imidazolinium and diazonium.

Claims Text - CLTX (8):

6. The method as described in claim 2 wherein either the first or **second** reactive compound bears a plurality of ionic groups selected from the group consisting of thioarylates, thioalkylates, arylates, alkylates and carboxylates.

Claims Text - CLTX (18):

16. The method as described in claim 3 wherein the semi-permeable **membrane** is selected from the group consisting of cellulose acetate, polysulfone and polyamide.

Claims Text - CLTX (19):

17. The method as described in claim 2 wherein the semi-permeable **membrane** is cellulose triacetate and further comprising removing essentially all water from the **membrane** by solvent extraction or freeze drying following Step (b).

Claims Text - CLTX (20):

18. The method as described in claim 12 wherein the charge density of the **second** reactive compound is greater than the charge density of the first reactive compound.

Claims Text - CLTX (21):

19. The method as described in claim 16 wherein either the first or **second** reactive compound is a vinyl addition polymer containing at least about 1 mole percent of methacrylic acid, acrylic acid or crotonic acid.

Claims Text - CLTX (24):

22. The method as described in claim 21 wherein the methacrylic acid polymer is the first reactive compound and the **second** reactive compound is a vinyl addition polymer derived from: (a) about 1 to about 50 mole percent of a monomer corresponding to the formula ##STR63## wherein R.sup.1 at each occurrence is a C.sub.1 to C.sub.4 alkyl or both R.sup.1 groups together with --S+&lt; form a 5-, 6- or 7-membered ring and A.sup.- is a compatible anion and (b) a remaining amount of one or more methacrylate or acrylate esters or monomers of the formula ##STR64## wherein D is a C.sub.8 to C.sub.20 or ##STR65##

Claims Text - CLTX (26):

24. The method as described in claim 23 further comprising contacting the **membrane** after Step (b) with the first reactive ionic compound in an aqueous diluent while maintaining a chemical potential gradient.

Claims Text - CLTX (27):

25. The method as described in claim 21 wherein the methacrylic acid polymer is the **second** reactive compound and the first reactive compound is a vinyl addition polymer derived from: (a) about 1 to about 50 mole percent of a monomer corresponding to the formula ##STR66## wherein R.sup.1 at each occurrence is a C.sub.1 to C.sub.4 alkyl or both R.sup.1 groups together with --S&lt;+ form a 5-, 6- or 7-membered ring and A.sup.- is a compatible anion and (b) a remaining amount of one or more methacrylate or acrylate esters or monomers of the formula ##STR67## wherein D is a C.sub.8 to C.sub.20 alkyl or ##STR68##

US Reference US Original Classification - UROR  
(37):

**210/500.42**

US Reference Group - URGP (37):

4705636 19871100 Small et al. **210/500.42**